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Heremans et al.

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(54) **THERMOELECTRIC DEVICE UTILIZING NON-ZERO BERRY CURVATURE**

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(22) Filed: **Oct. 11, 2018**

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Related U.S. Application Data

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H01L 37/00 (2006.01)

(52) **U.S. Cl.**
CPC ***H01L 37/00*** (2013.01)

(58) **Field of Classification Search**
CPC H01L 37/00; H01L 35/12; H01L 35/14
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,653,548	B2 *	11/2003	Yamashita	H01L 35/18 136/201
2010/0139730	A1 *	6/2010	Bentien	C30B 15/00 136/201
2016/0372650	A1 *	12/2016	Ghoshal	F25B 21/02
2018/0366633	A1 *	12/2018	Fu	H01L 35/32
2019/0067547	A1 *	2/2019	Gooth	H01L 35/00

OTHER PUBLICATIONS

Chen et al. “Thermoelectric transport in double-Weyl semimetals”. Phys. Rev. B 93, 155125. Apr. 14, 2016. (Year: 2016).*
Lundgren et al. “Thermoelectric properties of Weyl and Dirac semimetals”. Phys. Rev. B 90, 165115. 2014. (Year: 2014).*
Das et al. “Berry curvature induced thermopower in type-I and type-II Weyl semimetals”. Phys. Rev. B 100, 085406. 2019. (Year: 2019).*

* cited by examiner

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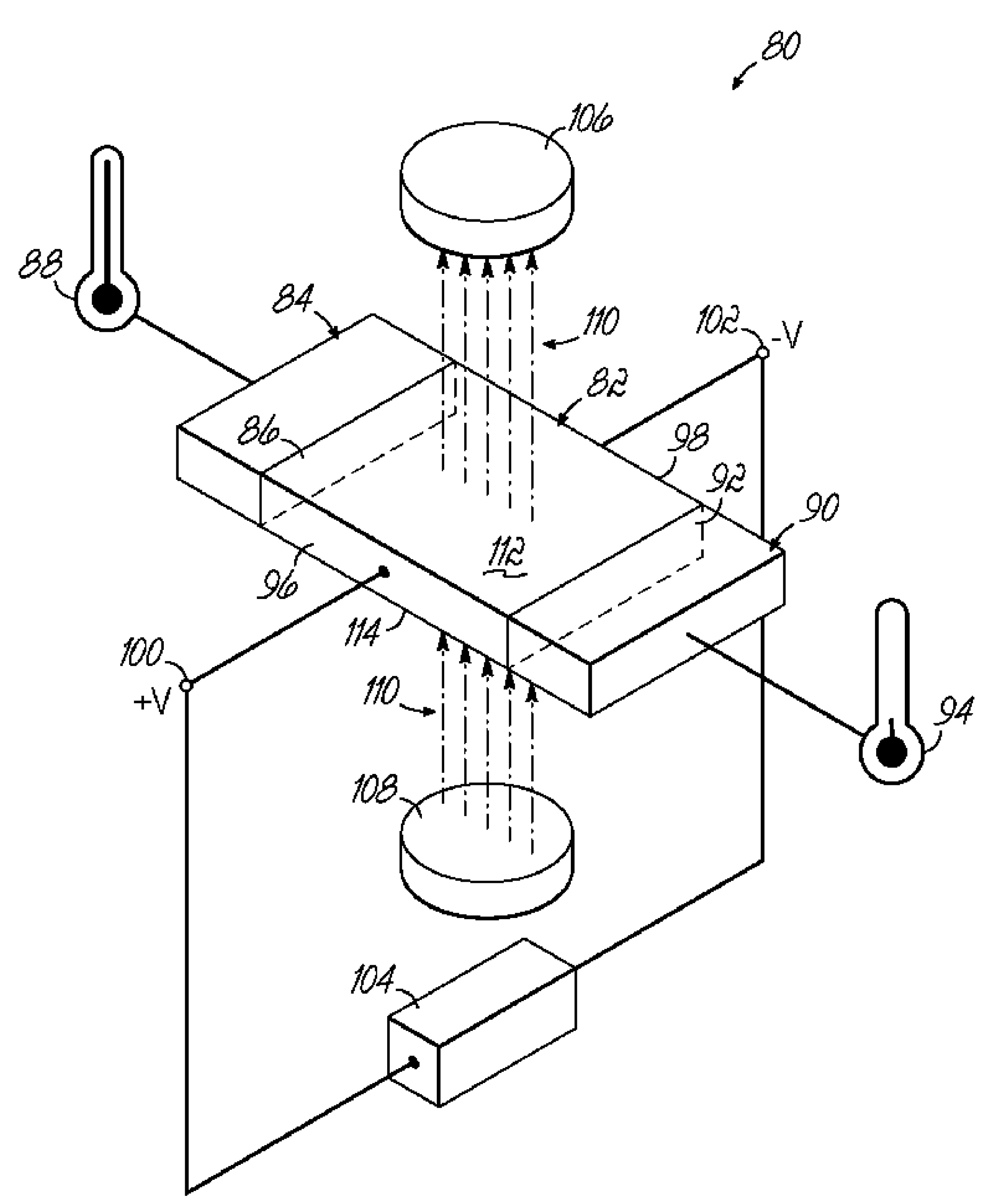
(57) **ABSTRACT**

Thermoelectric devices and methods of using thermoelectric devices. A thermoelectric device includes a thermoelectric element comprised of a material having a non-zero Berry curvature. The device may operate as a Nernst generator that generates electricity in response to application of a temperature gradient to the thermoelectric element, or as an Ettingshausen cooler that pumps heat into or out of an object to be heated or cooled in response to application of a current to the thermoelectric element. In either application, the non-zero Berry curvature of the material allows the device to operate without an externally applied magnetic field.

5 Claims, 11 Drawing Sheets



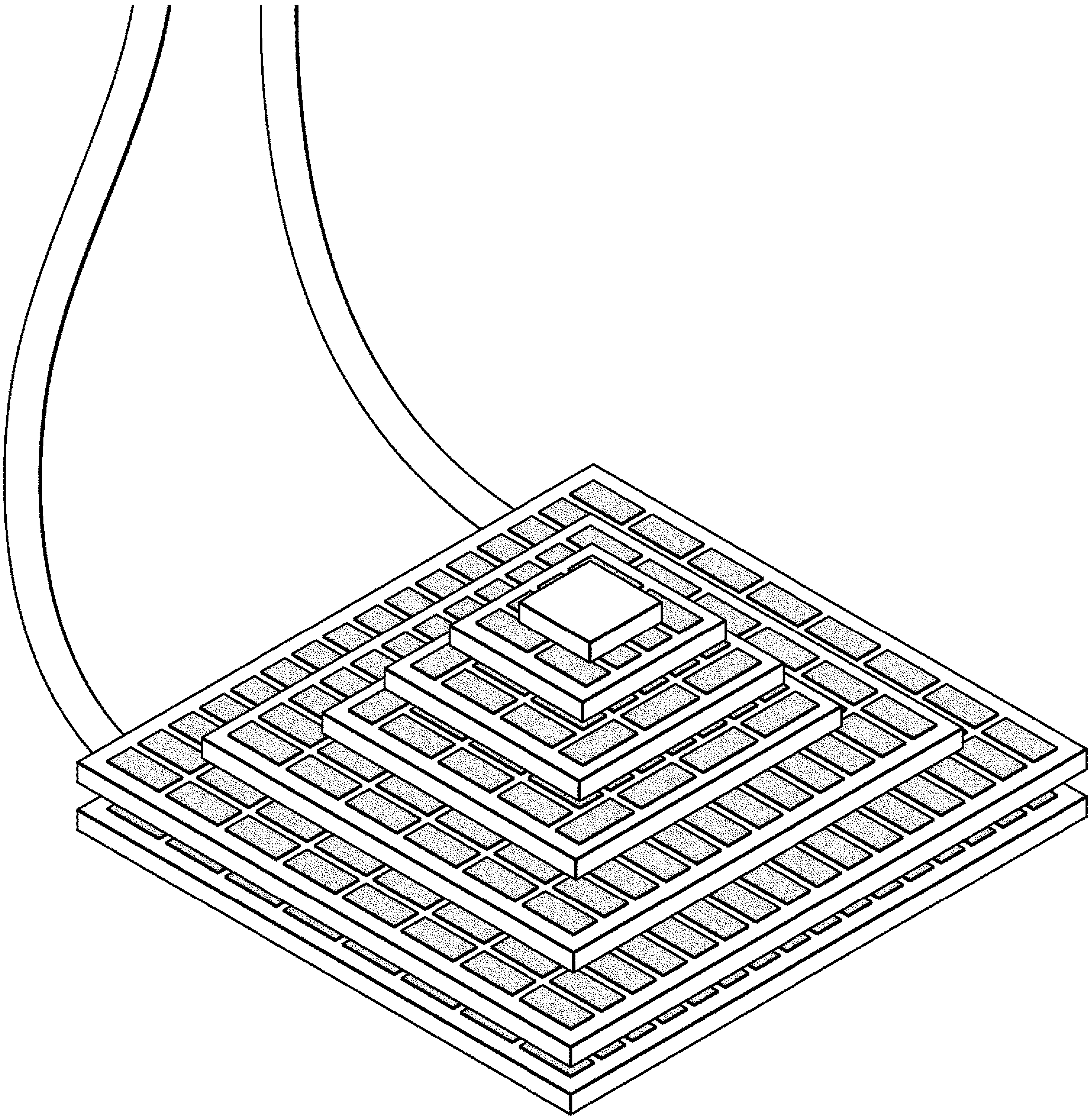


FIG. 1
PRIOR ART

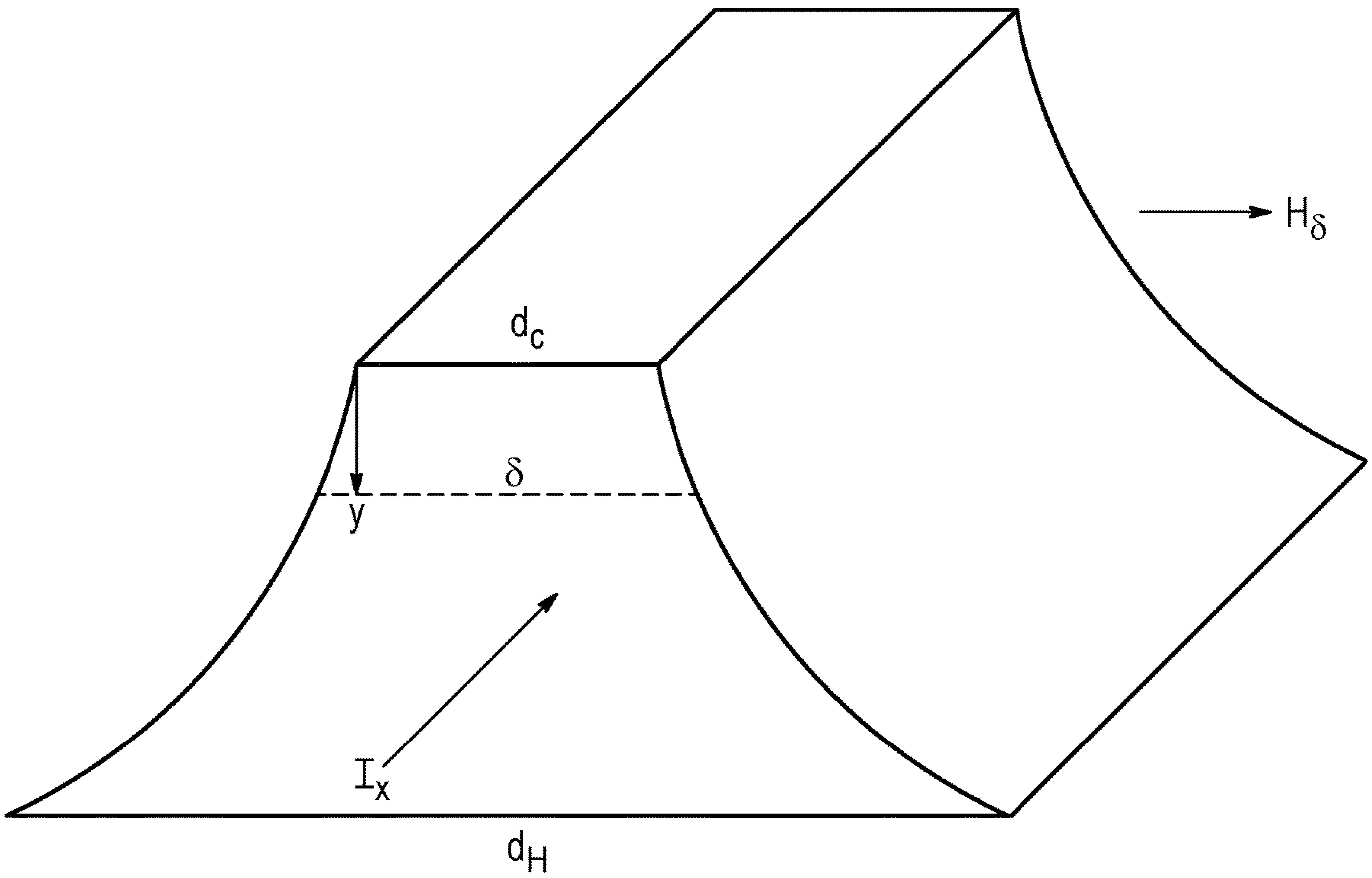


FIG. 2
PRIOR ART

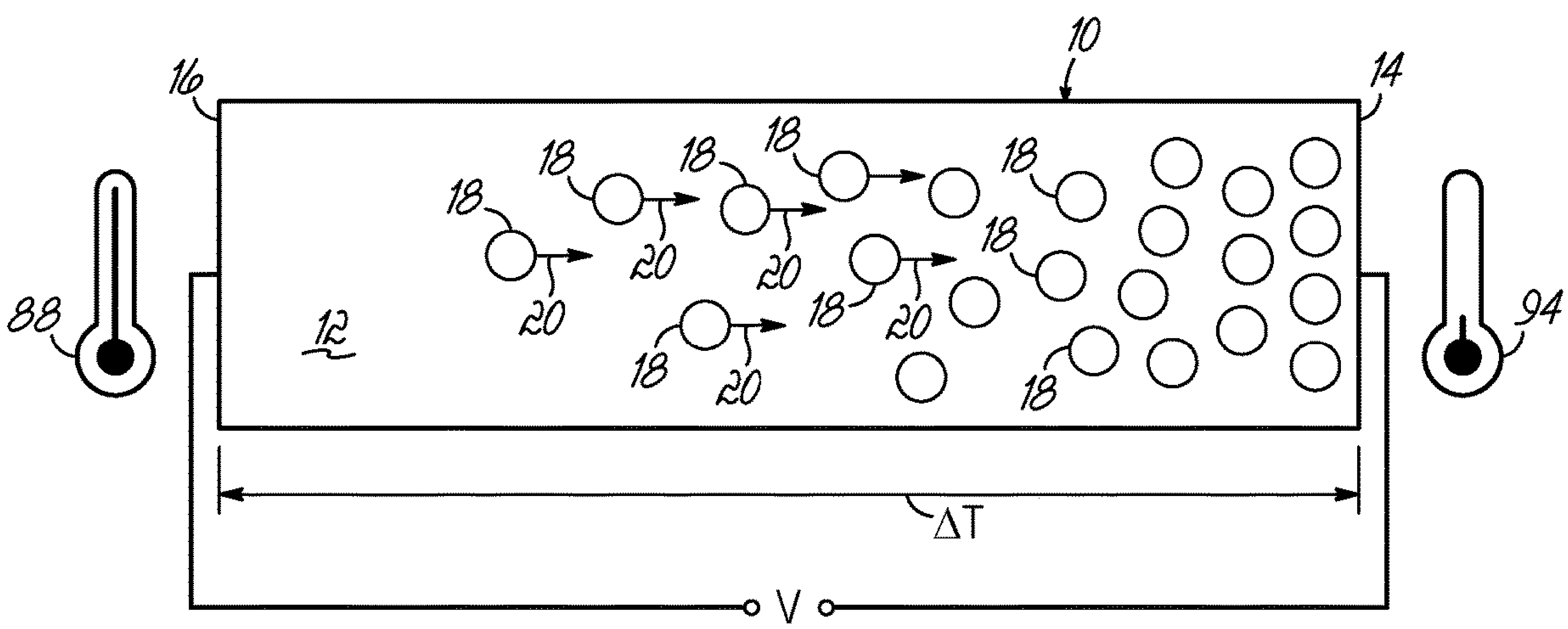
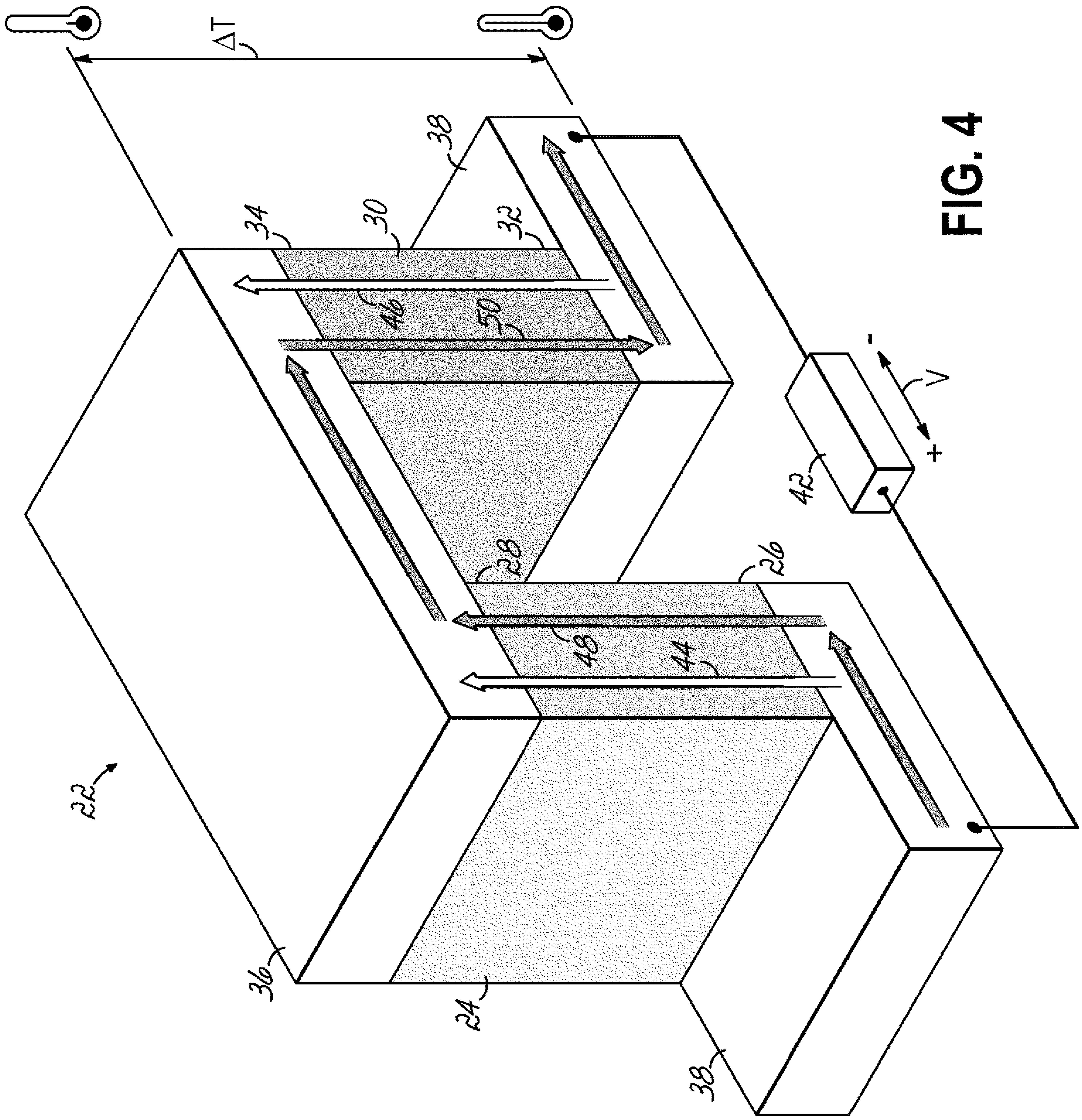


FIG. 3



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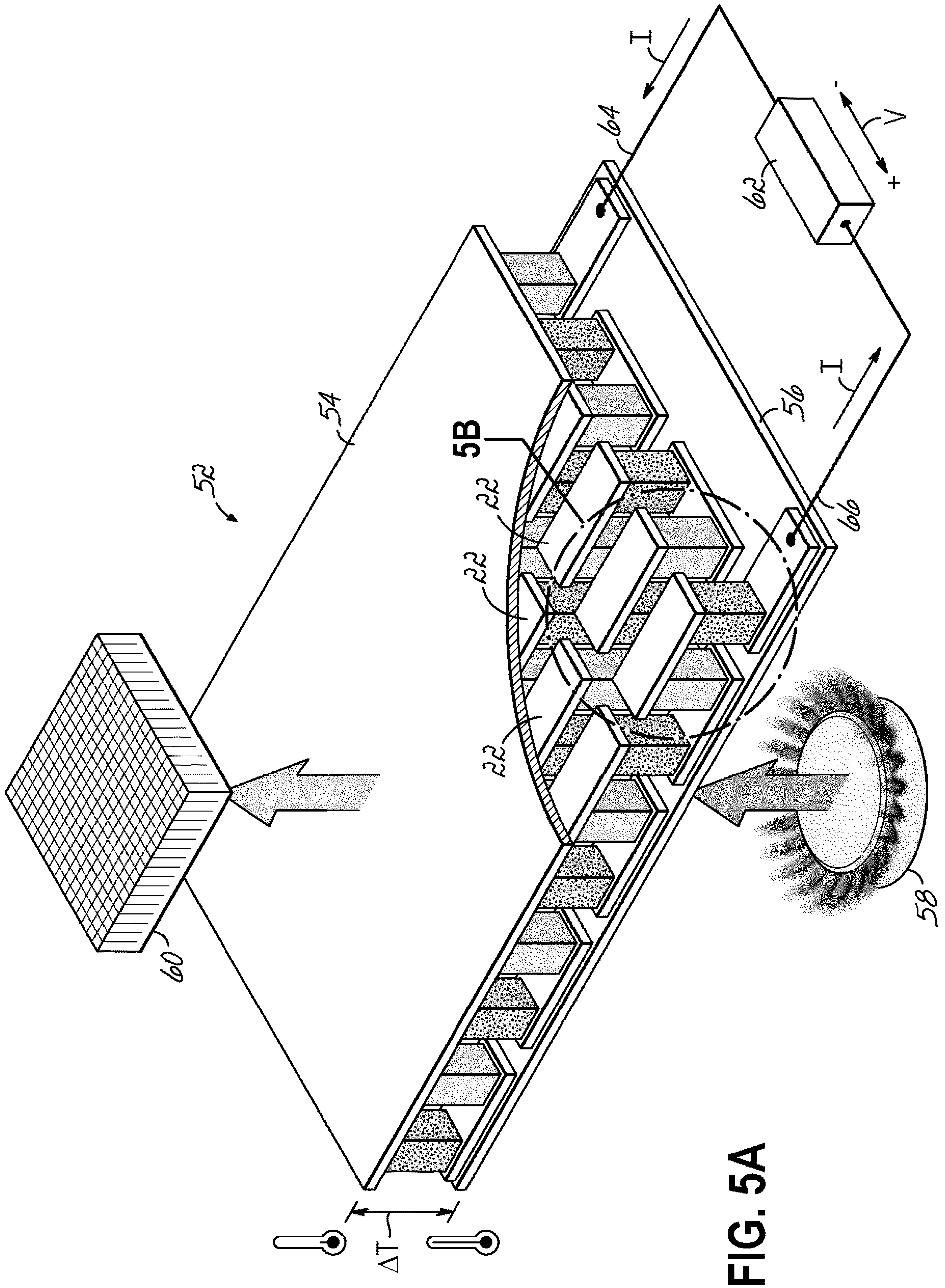

FIG. 5A

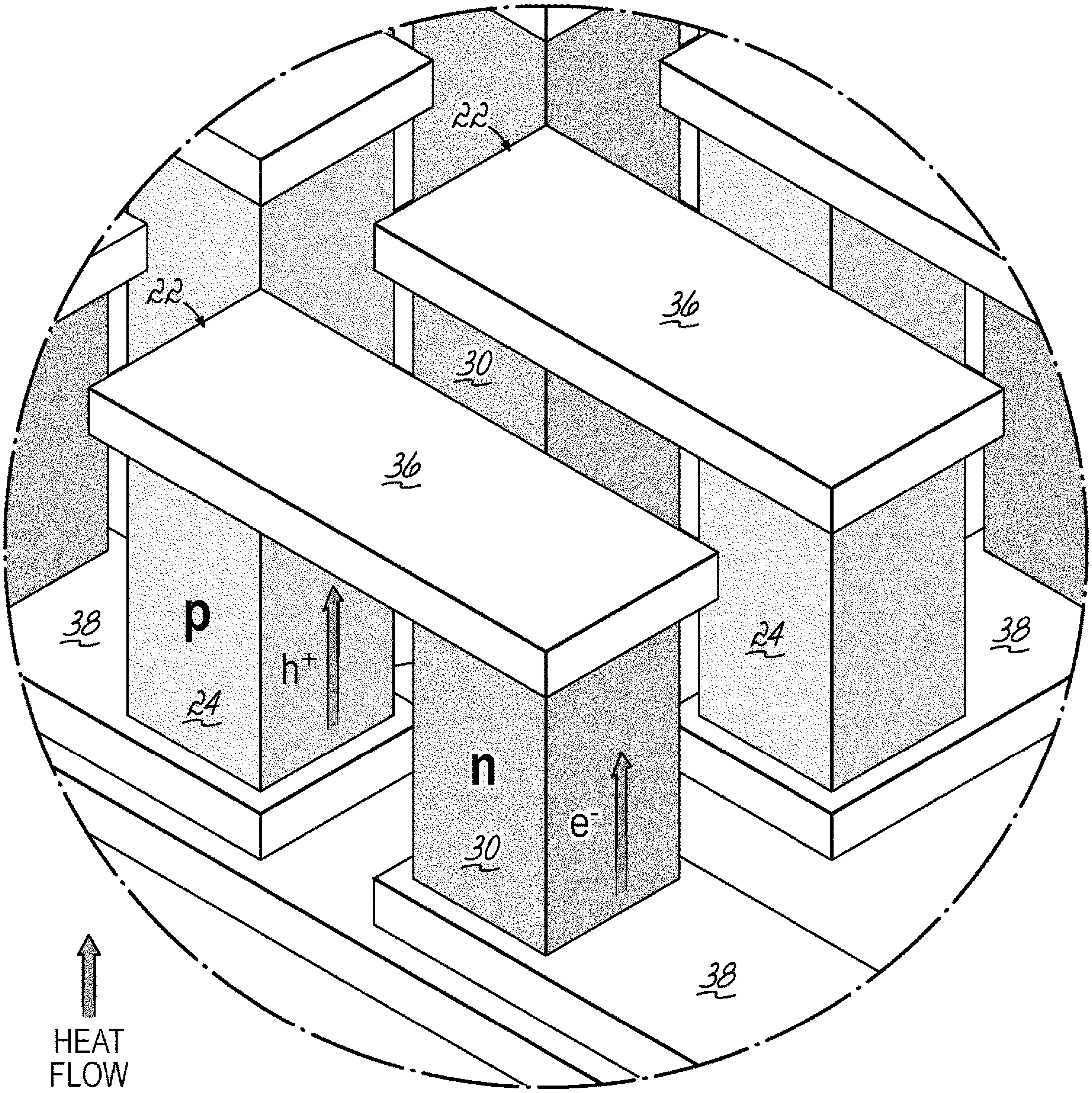

FIG. 5B

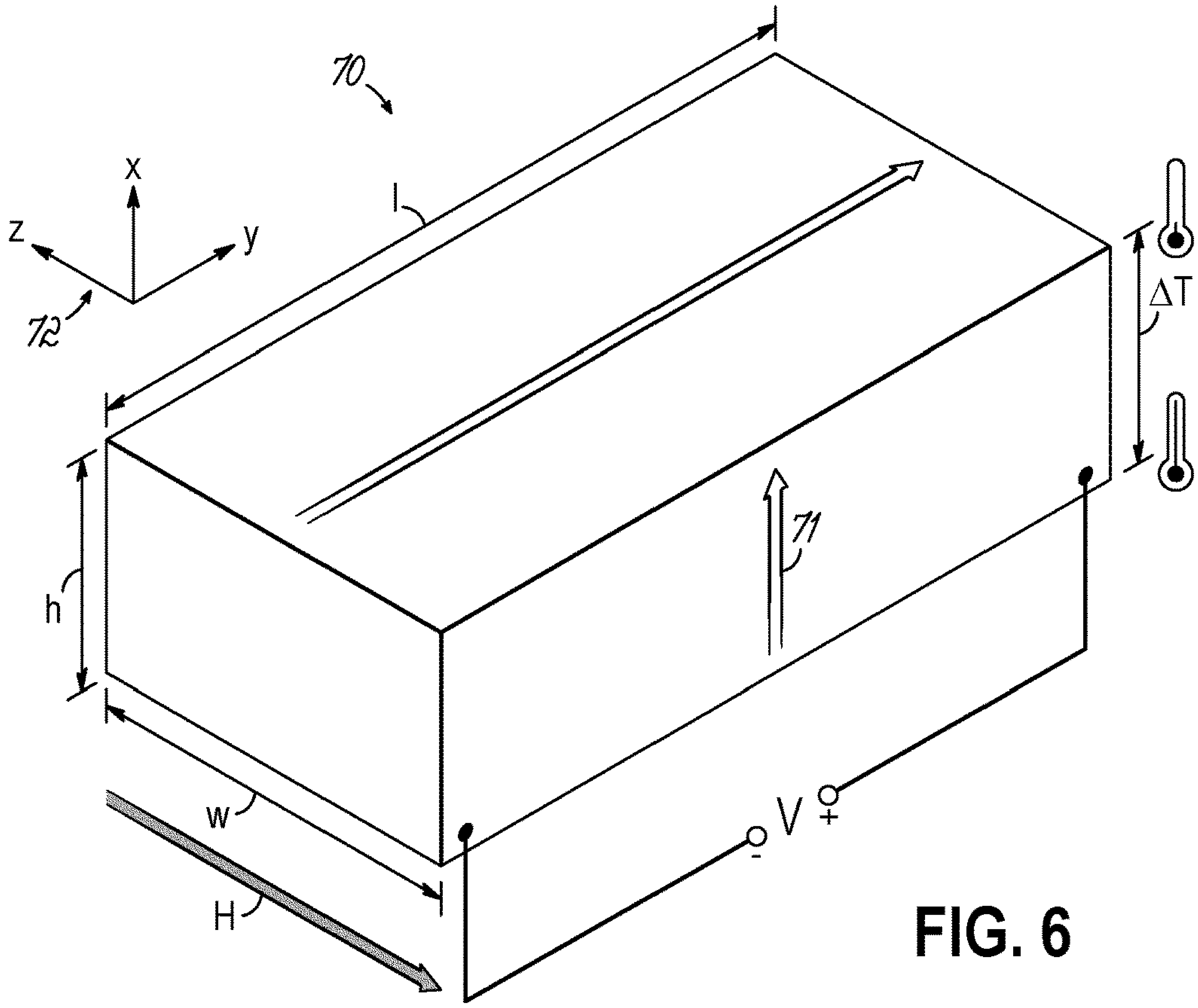

FIG. 6

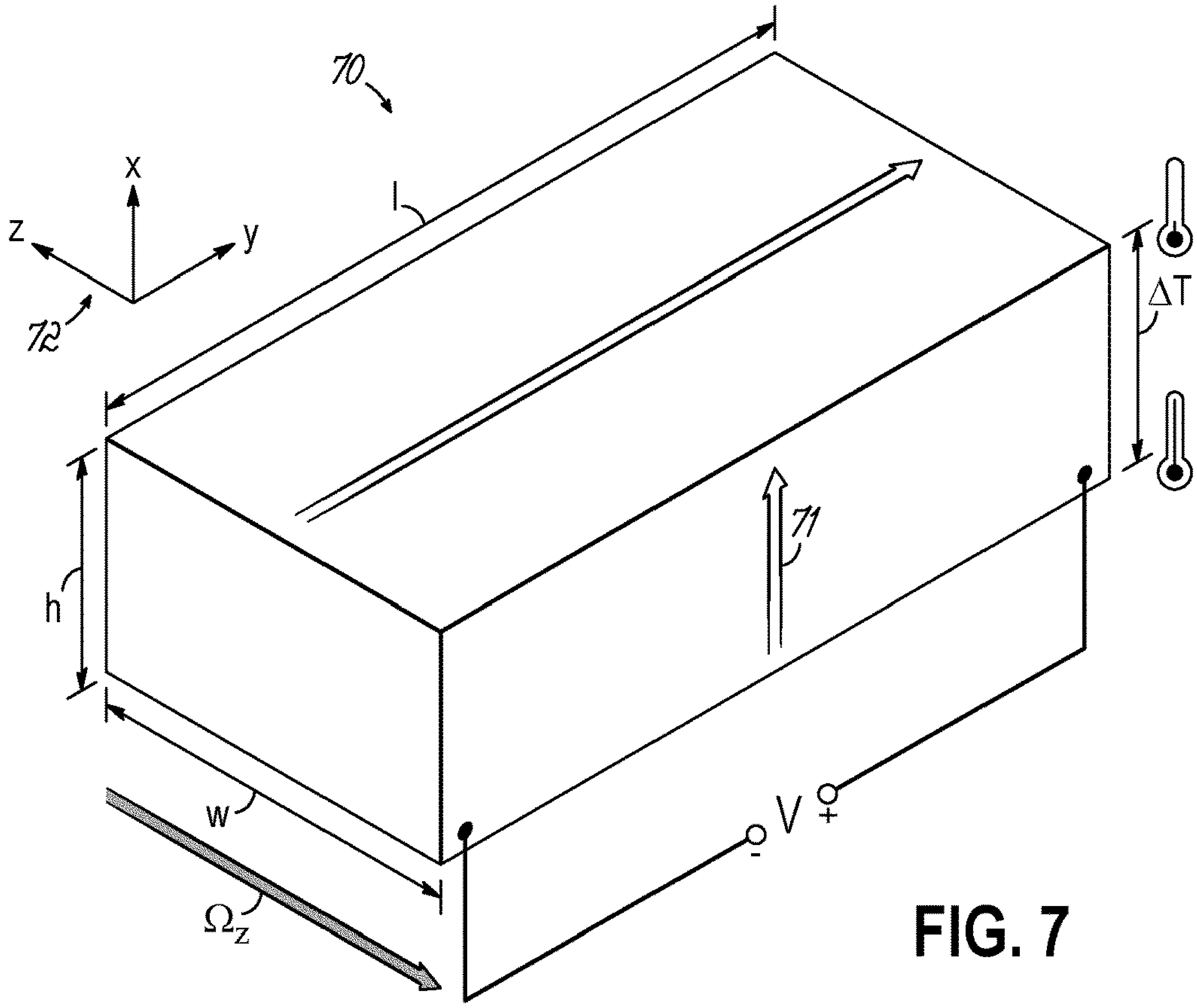

FIG. 7

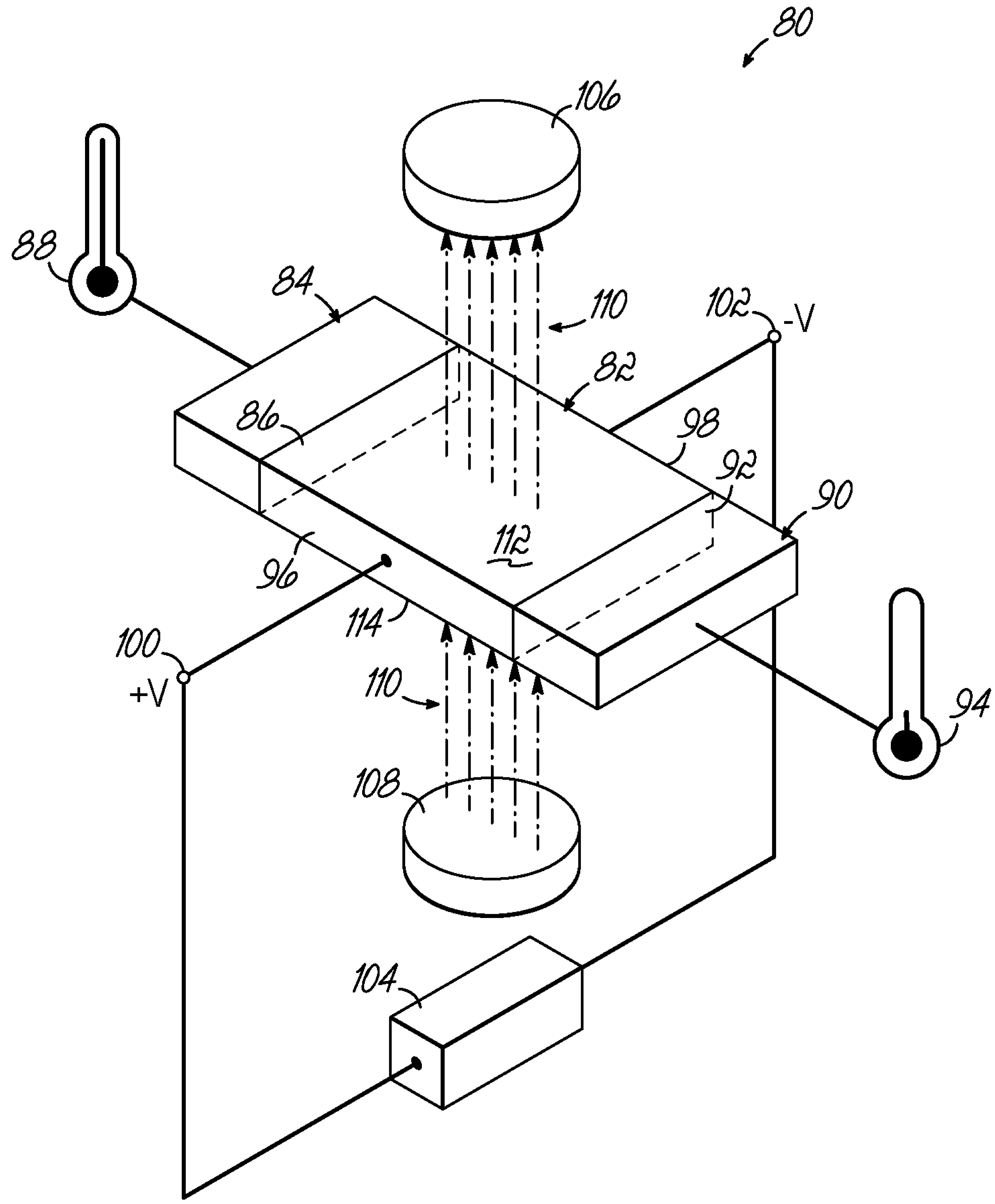

FIG. 8

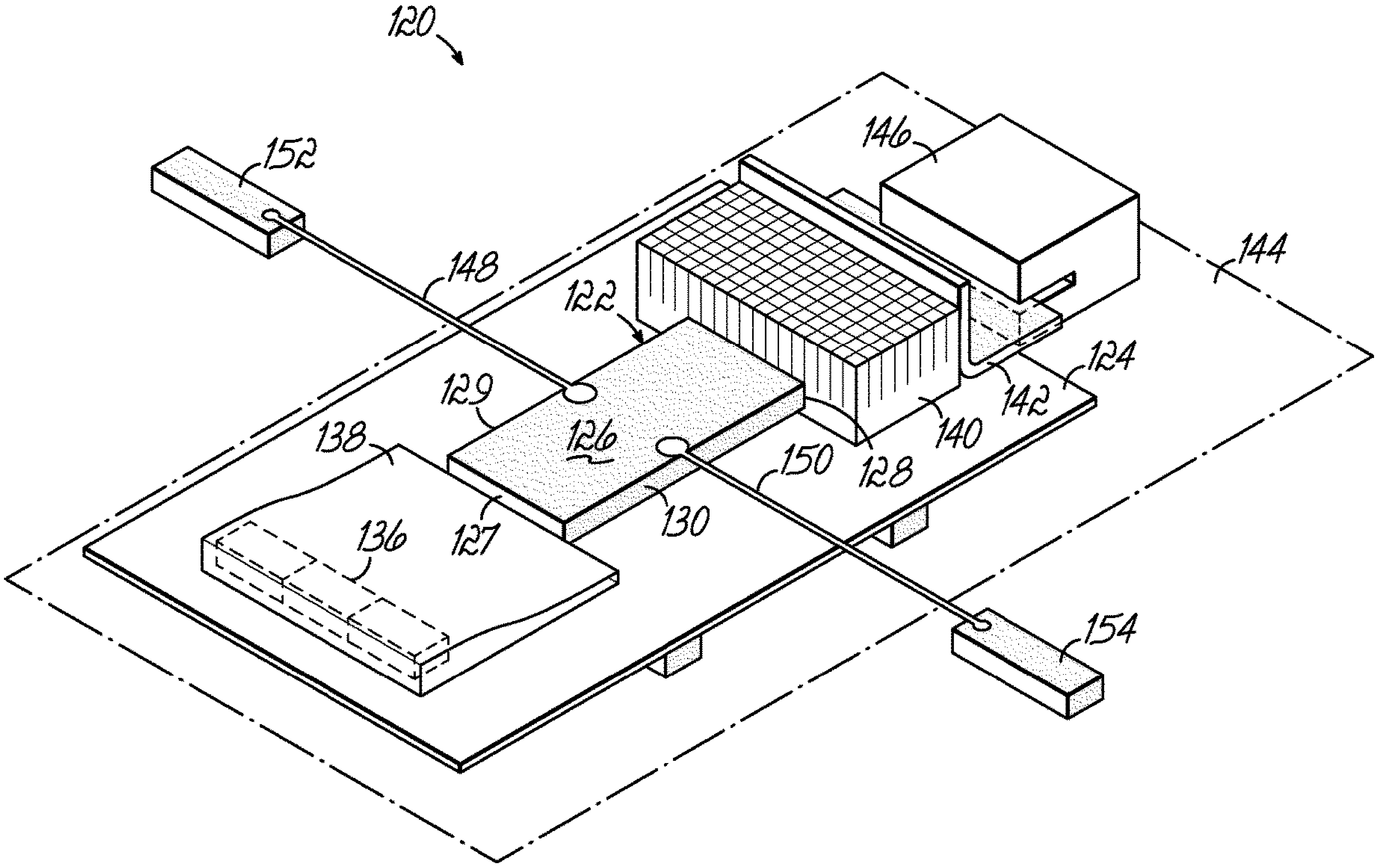
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FIG. 9

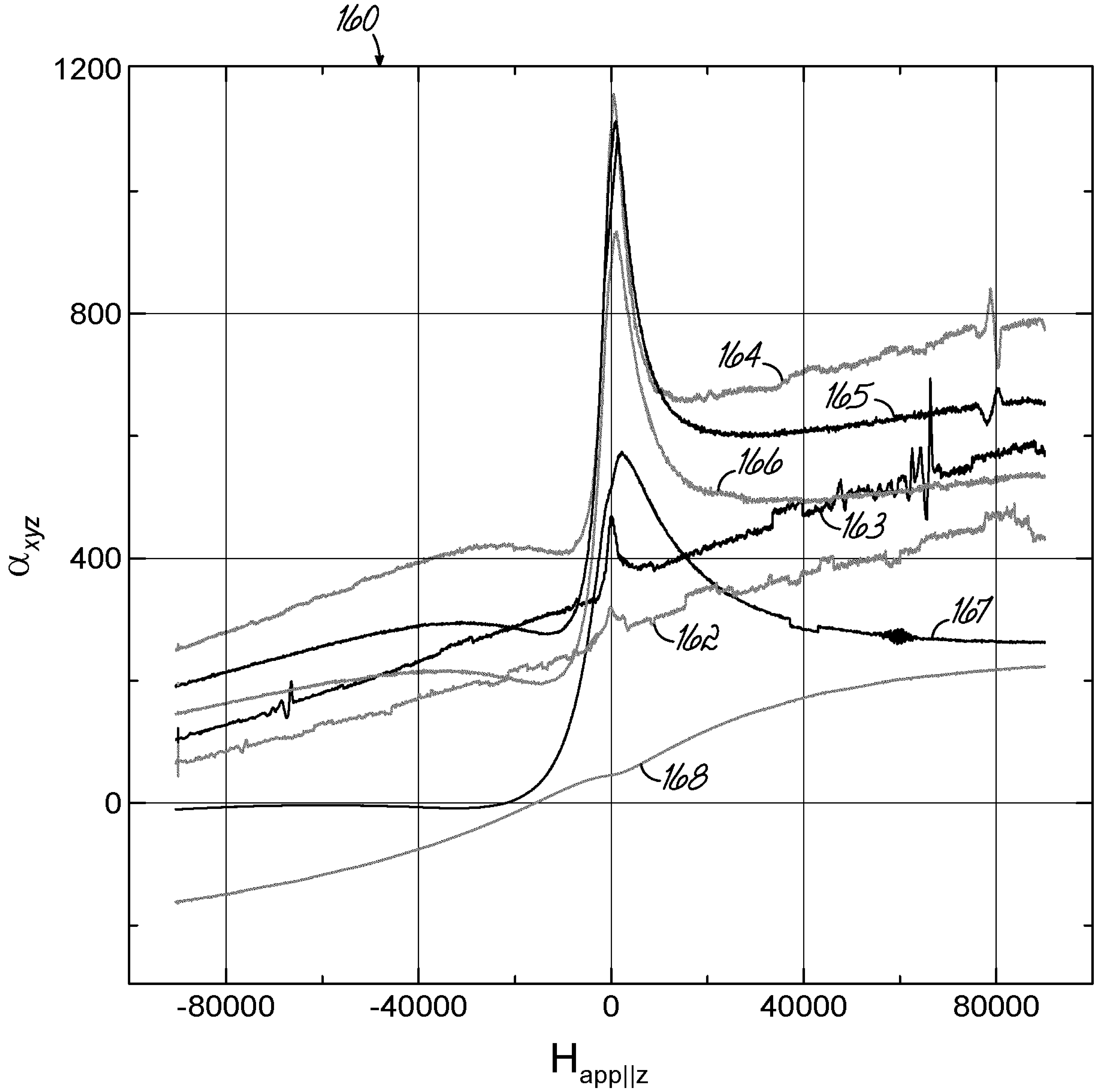
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FIG. 10

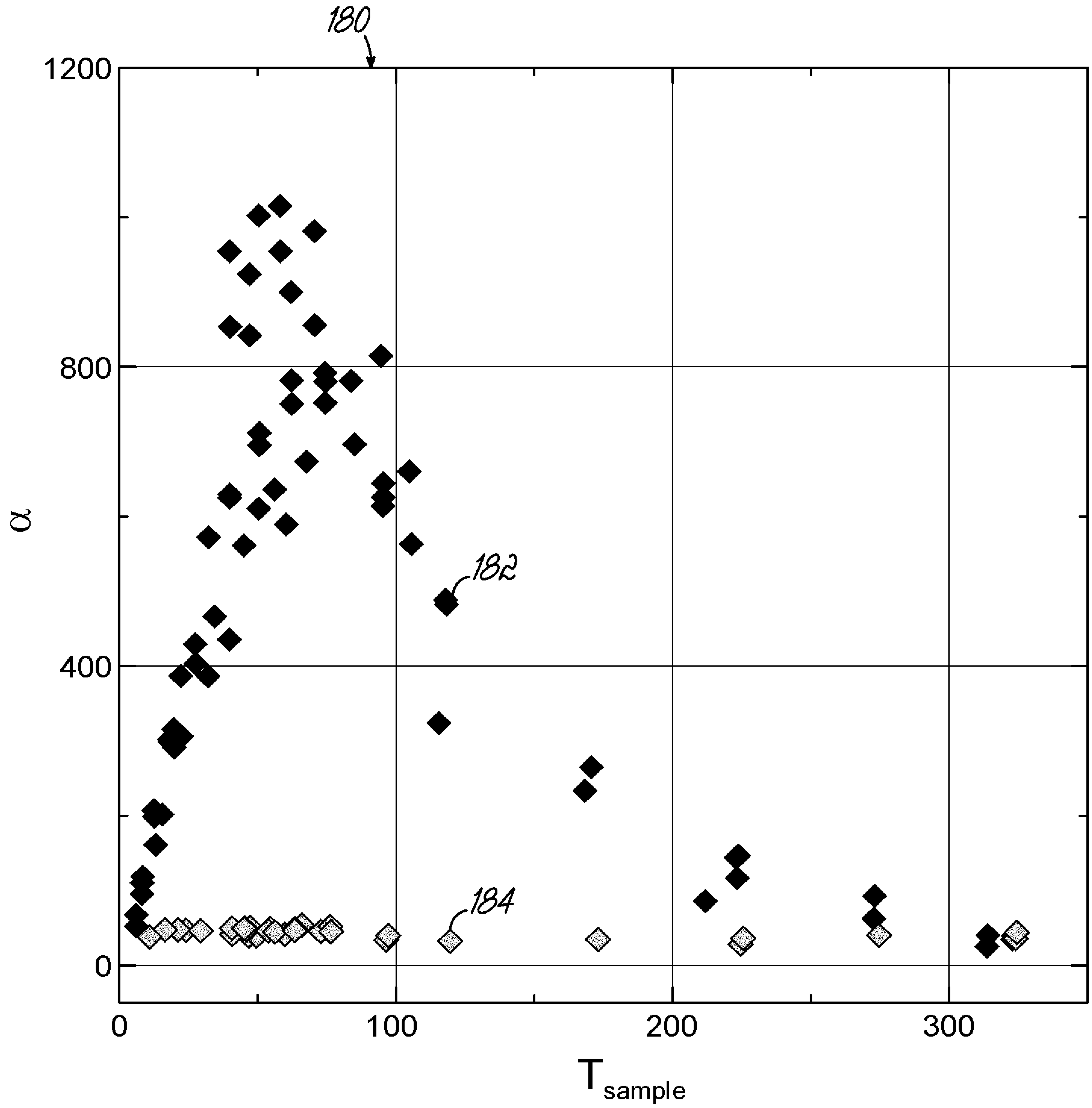

FIG. 11

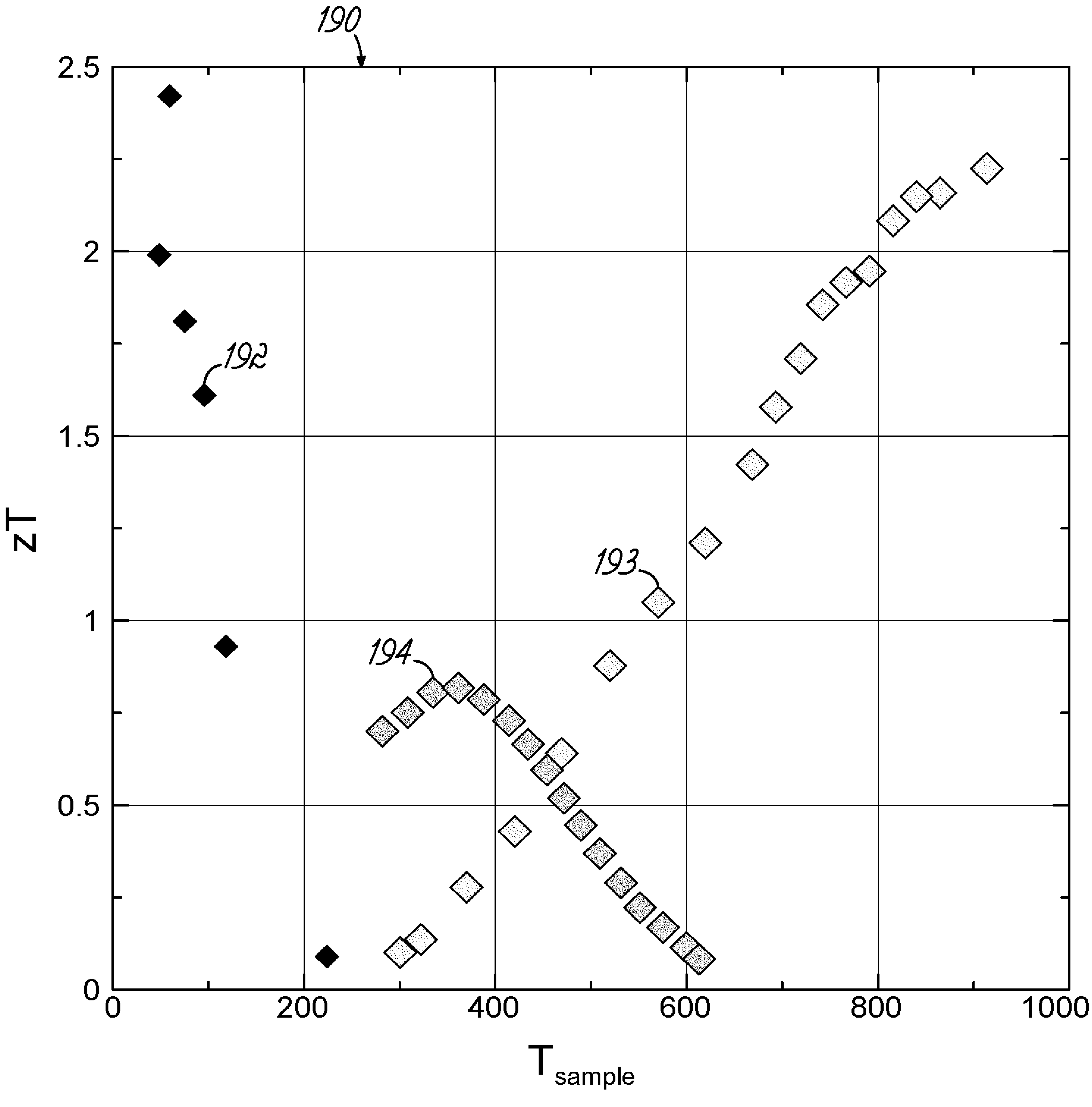

FIG. 12

THERMOELECTRIC DEVICE UTILIZING NON-ZERO BERRY CURVATURE

This application claims the benefit of U.S. Application No. 62/570,782 filed on Oct. 11, 2017 and entitled "Thermoelectric Device Using Weyl Semimetal", the disclosure of which is incorporated by reference herein in its entirety.

BACKGROUND

It is estimated that in 2017, the United States consumed 97.7 quads providing for its residential, commercial, industrial, and transportation energy needs. Approximately 80% of this energy was produced by fossil fuels such as petroleum (37.1%), natural gas (28.7%), and coal (14.3%). Nuclear power (8.62%) and biomass (5.03%) accounted for another 13.7% of the energy produced. The approximately 6% remaining was generated from sources such as hydroelectric, wind, geothermal, and solar. Of the energy consumed, it is further estimated that only 32% produced useful work, with the remaining 68% being rejected into the environment as waste heat. Transportation applications are particularly inefficient, with about 79% of the energy consumed producing waste heat. Recovery of even a portion of this waste heat could significantly reduce the amount of energy consumed.

Attempts to recover energy from waste heat include using the heat to generate electricity. For example, waste heat may be used to vaporize liquids or heat gases that are provided to an engine which powers an electric generator. Another approach to generating electricity from waste heat is to use the waste heat to produce a temperature gradient across a thermoelectric device that produces electricity through a thermoelectric effect.

Thermoelectric devices include thermoelectric generators, Peltier devices, and Nernst/Ettingshausen devices. Conventional thermoelectric devices include thermoelectric generators that generate electricity from a temperature gradient and Peltier devices such as thermoelectric heat-pumps (also referred to as Peltier coolers or thermoelectric coolers) that use an applied current to generate a temperature gradient. Thermoelectric generators and Peltier devices have a longitudinal geometry in which the temperature gradient and induced voltage run parallel to one another. Conventional longitudinal thermoelectric devices require both n-type and p-type materials electrically connected in series and thermally connected in parallel. To increase efficiency, Peltier devices are often cascaded (e.g., stacked with increasingly smaller surface areas on top) as shown in FIG. **1**. The need for electrical connections between the n-type and p-type materials, as well as the need for this cascading in Peltier devices, add to the cost and complexity of conventional, longitudinal thermoelectric devices.

Nernst/Ettingshausen devices are solid-state devices where an applied temperature gradient and perpendicular magnetic field generate a mutually orthogonal voltage, or an applied current and perpendicular magnetic field generate a mutually orthogonal temperature gradient. The magnetic field generates a skew force (Lorentz force) that accelerates charge carriers in a direction perpendicular to the temperature gradient in the device. As with Peltier devices, Nernst/Ettingshausen devices include thermoelectric heat-pumps (also referred to as Ettingshausen coolers) that use an applied current to generate a temperature gradient, and thermoelectric generators (also referred to as Nernst generators) that generate electricity from a temperature gradient. Nernst/Ettingshausen devices utilize a transverse geometry and thus only require one polarity of material.

To increase efficiency, Nernst/Ettingshausen devices may be shaped as shown in FIG. **2**. Because the shaping is done on the thermoelectric material itself, this technology is more simplistic than that of Peltier devices and eliminates losses due to the multiple electrical connections of n-type and p-type thermoelectric materials. However, unlike Peltier devices, conventional Nernst/Ettingshausen devices require an externally applied magnetic field that is orthogonal to the electrical current and temperature gradient. The magnetic fields used in conventional Nernst/Ettingshausen devices must be relatively intense, which can make Nernst/Ettingshausen devices impractical for commercial applications.

Thus, there is a need for improved thermoelectric devices and methods of using thermoelectric devices to provide thermoelectric electricity generation and/or cooling with improved efficiency that do not require different types of materials or intense externally applied magnetic fields.

SUMMARY

In an embodiment of the invention, a thermoelectric device is provided comprising a thermoelectric element including a material having a non-zero Berry curvature.

In an aspect of the invention, the thermoelectric element may be configured to generate a voltage in response to being exposed to a temperature gradient.

In another aspect of the invention, the thermoelectric element may be configured to generate a temperature gradient in response to application of an electrical current.

In another aspect of the invention, the non-zero Berry curvature may be along an axis of the material orthogonal to a temperature gradient to which the thermoelectric element is exposed or the thermoelectric element generates.

In another aspect of the invention, the thermoelectric element may have a first side, a second side located a first distance from the first side along a first dimension, a third side that intersects the first and second sides, and a fourth side located a second distance from the third side along a second dimension orthogonal to the first dimension and that intersects the first and second sides. The thermoelectric device may further include a first thermal coupler configured to thermally couple the first side to a heat source and a second thermal coupler configured to thermally couple the second side to a heat sink. A voltage may be generated between the third and fourth sides in response to application of a temperature gradient between the first thermal coupler and the second thermal coupler.

In another aspect of the invention, the thermoelectric device may include a magnet configured to provide a magnetic field to the thermoelectric element.

In another aspect of the invention, the thermoelectric device may be one of a Ettingshausen cooler or a Nernst generator.

In another aspect of the invention, the material may be a Weyl semimetal.

In another aspect of the invention, the Weyl semimetal may break time-reversal symmetry.

In another embodiment of the invention, a method of generating electricity is provided. The method includes providing a temperature gradient across a thermoelectric element including a material having a non-zero Berry curvature.

In an aspect of the invention, providing the temperature gradient across the thermoelectric element may include coupling the first side of the thermoelectric element to the

heat source and coupling the second side of the thermoelectric element to the heat sink, wherein the second side may be located the first distance from the first side along the first dimension.

In another aspect of the invention, the method may further include applying the magnetic field to the thermoelectric element.

In another aspect of the invention, the method may include orienting the thermoelectric element so that the axis of the material having the non-zero Berry curvature is orthogonal to the temperature gradient.

In another embodiment of the invention, a method of generating a temperature gradient is provided. The method includes passing a current through the thermoelectric element including the material having the non-zero Berry curvature.

In another aspect of the invention, generating the temperature gradient may include coupling the first side of the thermoelectric element to the heat sink, and coupling the second side of the thermoelectric element to an object to be cooled or warmed, wherein the second side is located the first distance from the first side along the first dimension.

In another aspect of the invention, the method may include applying the magnetic field to the thermoelectric element.

In another aspect of the invention, passing the current through the thermoelectric element from the third side to the fourth side may cool the object, and passing the current from the fourth side to the third side may warm the object.

In another aspect of the invention, the method may include orienting the thermoelectric element so that the axis of the material having the non-zero Berry curvature is orthogonal to the temperature gradient and the current.

The above summary presents a simplified overview of some embodiments of the invention to provide a basic understanding of certain aspects of the invention discussed herein. The summary is not intended to provide an extensive overview of the invention, nor is it intended to identify any key or critical elements, or delineate the scope of the invention. The sole purpose of the summary is merely to present some concepts in a simplified form as an introduction to the detailed description presented below.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate various embodiments of the invention and, together with the general description of the invention given above, and the detailed description of the embodiments given below, serve to explain the embodiments of the invention.

FIG. **1** is an isometric view of a Peltier device having a cascaded configuration.

FIG. **2** is an isometric view of an Nernst/Ettingshausen device configured to have a cross-sectional area that varies along the length of a temperature gradient applied across the device.

FIG. **3** is a diagrammatic view of a thermoelectric element depicting movement of charge carriers in response to a temperature gradient across the element.

FIG. **4** is an isometric view of a longitudinal thermoelectric module that utilizes two thermoelectric elements of FIG. **3** to generate a voltage based on the Seebeck effect.

FIG. **5**A is an isometric view of a thermoelectric generator including a plurality of the thermoelectric modules of FIG. **4**.

FIG. **5**B is an enlarged view of a portion of the thermoelectric generator of FIG. **5**A showing additional details thereof.

FIG. **6** is an isometric view of a transverse thermoelectric element that utilizes the Nernst effect to generate a voltage from a temperature gradient.

FIG. **7** is an isometric view of the thermoelectric element of FIG. **6** showing a spatial relationship between a crystallographic axis of the thermoelectric element along which a non-zero Berry curvature exists, the temperature gradient applied to the thermoelectric element, and the voltage produced by the thermoelectric element.

FIG. **8** is a diagrammatic view of an exemplary transverse thermoelectric generator, or Nernst generator, including the thermoelectric element of FIG. **7**.

FIG. **9** is an isometric view of a thermoelectric test device used to collect Nernst effect performance data on the thermoelectric element of FIG. **7**.

FIG. **10** is graphical view illustrating the Nernst thermopower verses applied magnetic field at different operating temperatures.

FIG. **11** is graphical view illustrating Nernst thermopower as a function of temperature in the absence of an applied magnetic field for a thermoelectric element having a transverse geometry.

FIG. **12** is a graphical view illustrating thermoelectric figures of merit verses temperature for different thermoelectric materials in transverse and longitudinal configurations without an externally applied magnetic field.

DETAILED DESCRIPTION

Conventional thermoelectric devices use a longitudinal geometry and depend on the Seebeck effect to generate electricity from waste heat. Thermoelectric devices having transverse geometries have significant advantages in cost and complexity over those having a longitudinal geometry. However, because conventional transverse thermoelectric devices depend on the Nernst effect to generate electricity, they normally need a large externally applied magnetic field to function. Embodiments of the invention provide the advantages of transverse geometries in thermoelectric devices having little or no need for an external magnetic field. This improvement in thermoelectric devices has been achieved by using thermoelectric materials that have a non-zero Berry curvature, such as found in certain Weyl semimetals.

A Weyl semimetal is a material having inverted conduction and valence bands where the bands are linear Dirac bands near the crossing points. The breaking of time-reversal symmetry or spatial-inversion symmetry may lift the degeneracy of the band crossing points, giving rise to pairs of Weyl nodes. Separated Weyl nodes may result when the electron band structure of the material has singly degenerate bands that include bulk band crossings known as "Weyl points". Electrons around the Weyl points have a property called Berry curvature Ω_z that behaves like an internal magnetic field. The Berry curvature Ω_z may give electrons an additional velocity that is normal to the direction of their momentum. One Weyl semimetal that breaks time-reversal symmetry and has a non-zero Berry curvature is $YbMnBi_2$. A thermoelectric device made from $YbMnBi_2$ in accordance with an embodiment of the invention has demonstrated previously unknown thermoelectric efficiency in a transverse geometry without the need for an externally applied magnetic field. Use of materials having non-zero

Berry curvatures thereby provides transverse thermoelectric devices with significant advantages in cost and reliability over conventional devices.

Embodiments of the invention may utilize the transverse geometry and cascaded shape of conventional Nernst/Ettingshausen devices, but do not require an externally applied magnetic field. Weyl semimetals having a non-zero net Berry curvature may be used to form these new Nernst/Ettingshausen devices. The non-zero Berry curvature may act as an intrinsic magnetic field in k-space, generating a skew force to the applied current and thus inducing a temperature gradient. Materials with a non-zero Berry curvature may allow thermoelectric devices to be built with the simplicity of the Nernst/Ettingshausen geometry without the need for an externally applied magnetic field. Thermoelectric devices made in accordance with embodiments of the invention also provide previously unheard of thermoelectric figures of merit in a transverse geometry.

FIG. **3** depicts a cross-sectional view of a thermoelectric element **10** comprising a length of thermoelectric material **12** having a cold end **14** and a hot end **16**. Application of heat to the thermoelectric element **10** that produces the depicted temperature difference ΔT may cause charge carriers **18** to migrate toward and/or condense at the cold end **14** of thermoelectric material **12** as indicated by the single headed arrows **20**. This phenomenon is known as the Seebeck effect.

For a thermoelectric material **12** in which the majority carriers are positive charge carriers **18** (e.g., a p-type semiconductor), the carrier migration may cause a positive voltage V to build up across the length of the thermoelectric material **12** such that the cold end **14** has a higher potential than the hot end **16**. For a thermoelectric material **12** in which the majority carriers are negative charge carriers **18** (e.g., an n-type semiconductor), the carrier migration may cause a negative voltage V to build up across the thermoelectric material **12** such that the cold end **14** has a lower potential than the hot end **16**. The thermopower or Seebeck coefficient α of the length of thermoelectric material **12** is provided by:

$$\alpha = \frac{-E}{\nabla T} \qquad \text{Eqn. 1}$$

where E is the electric field and ∇T is the temperature gradient. Equation 1 may simplify to $\alpha = V/\Delta T$ when the voltage V and temperature difference ΔT are measured over the same length of material. Thus, Equation 1 may be used to determine an expected voltage that will be generated by the thermoelectric element **10** given the dimensions of the element. In order to define a consistent flow of current I that is independent of the type of charge carrier, current I is defined herein as always moving in the direction of positive charge flow. Thus, in materials having negative charge carriers **18**, current I flows in the opposite direction of the charge carriers **18**, and in materials having positive charge carriers **18**, the current I flows in the same direction as the charge carriers **18**.

It is typically desirable to use a thermoelectric material **12** with a relatively large Seebeck coefficient α in order to generate a higher voltage V for a given temperature difference ΔT than would be generated by a thermoelectric material with a low Seebeck coefficient α. A typical Seebeck coefficient α for a semiconductor may have a magnitude that ranges from 200 to 300 μV/K at room temperature. The thermoelectric efficiency of a thermoelectric material can be quantified by a dimensionless figure of merit zT given by:

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \qquad \text{Eqn. 2}$$

where T is the average absolute temperature of the thermoelectric element **10** in kelvin, σ is the electrical conductivity of the thermoelectric material **12**, κ is the thermal conductivity of the thermoelectric material **12**, and each of the parameters may vary with temperature.

According to Equation 2, the thermoelectric figure of merit zT is proportional to the electrical conductivity σ and the square of the Seebeck coefficient α, and inversely proportional to the thermal conductivity κ. A low thermal conductivity κ may enable a temperature gradient ∇T to be maintained across the thermoelectric element **10** with a lower flow of heat through the thermoelectric element **10** as compared to a high thermal conductivity κ. A high electrical conductivity σ may lower the impedance of the thermoelectric element **10**, thereby allowing it to source a larger amount of current I as compared to a thermoelectric element **10** with a low electrical conductivity σ.

It is normally desirable to use materials with as high of a thermoelectric figure of merit zT as possible. Useful devices may be made from thermoelectric materials with a thermoelectric figure of merit of 0.3. In contrast, a thermoelectric figure of merit of 1.0 is considered good, and a thermoelectric figure of merit of 2.0 or more is considered to be near the limit of what is possible with conventional technology. As can be seen from Equations 1 and 2, the voltage V generated by thermoelectric element **10** from a given temperature difference ΔT due to the Seebeck effect is limited by the intrinsic properties of the thermoelectric material **12**, e.g., the Seebeck coefficient α, electrical conductivity σ, and thermal conductivity κ.

The temperature difference ΔT may be generated by the thermoelectric element **10** itself in response to a current I being driven through the thermoelectric element **10**. Thus, the thermoelectric element **10** can be used as a heat pump by passing an externally sourced current I through the element. To generate the shown temperature difference ΔT in a thermoelectric material in which the majority carriers are positive charge carriers (e.g., holes), the current I may be driven from the cold end **14** toward the hot end **16**. In contrast, to generate the shown temperature difference ΔT in a thermoelectric material in which the majority carriers are negative charge carriers (e.g., electrons), the current I may be driven from the hot end **16** toward the cold end **14**.

FIG. **4** depicts a thermoelectric module **22** which utilizes the Seebeck effect and has a longitudinal geometry. Thermoelectric module **22** may include a thermoelectric element **24** made of a p-type thermoelectric material having a hot end **26** and a cold end **28**, a thermoelectric element **30** made of an n-type thermoelectric material having a hot end **32** and a cold end **34**, an upper electrode **36** coupling the cold end **28** of thermoelectric element **24** to the cold end **34** of thermoelectric element **30**, and lower electrodes **38** coupling the hot ends **26**, **32** of thermoelectric elements **24**, **30** to an electrical load **42**. Because the depicted type of thermoelectric module **22** relies on the Seebeck effect to generate electrical power, it uses thermoelectric elements **24**, **30** having different types of charge carriers and has an electrical output that scales intrinsically with the properties of the thermoelectric materials used in the thermoelectric elements **24**, **30**.

Application of a temperature difference ΔT across the thermoelectric module **22** may cause heat to flow from the hot ends **26**, **32** to the cold ends **28**, **34** of thermoelectric elements **24**, **30**, as indicated by single headed arrows **44**, **46**. The resulting temperature gradient ∇T may cause a flow of positive charge carriers from the hot end **26** to the cold end **28** of thermoelectric element **24** that results in a positive current flow toward the cold end **28**, as indicated by single headed arrow **48**. The temperature gradient ∇T may also cause a flow of negative charge carriers from the hot end **32** to the cold end **34** of thermoelectric element **30** that results in a positive current flow toward the hot end **32** as indicated by single headed arrow **50**. The electrodes **36**, **38** may be configured to complete the circuit, thereby allowing current to flow through the thermoelectric module **22** and electrical load **42**.

Because the voltage generated by thermoelectric module **22** is limited by the intrinsic properties of the thermoelectric materials from which it is made, thermoelectric generators using a longitudinal geometry are typically assembled from a large number of modules in order to produce a useful output voltage. FIGS. **5**A and **5**B depict an exemplary thermoelectric generator **52** including a plurality of thermoelectric modules **22** electrically coupled in a series configuration. The upper electrodes **36** of thermoelectric modules **22** are thermally coupled to an upper substrate **54**, and the lower electrodes **38** of thermoelectric modules **22** are thermally coupled to a lower substrate **56**. The thermoelectric modules **22** are thus thermally coupled to the upper and lower substrates **54**, **56** in parallel. The substrates **54**, **56** may be made from a material that has a low electrical conductivity, or is electrically isolated from the electrodes **36**, **38** by an electrically insulating layer (not shown), in order to avoid shorting out the thermoelectric generator **52**.

One of the substrates **54**, **56** (e.g., the lower substrate **56**) may be thermally coupled to a heat source **58** (e.g., the exhaust from combustion used to heat a boiler), and the other substrate **54**, **56** (e.g., the upper substrate **54**) may be thermally coupled to a heat sink **60** (e.g., a cooling medium such as the atmosphere or a reservoir of water). Thermally coupling the thermoelectric generator **52** between a heat source and a heat sink as described above may cause a temperature difference ΔT to develop across each of the thermoelectric modules **22**. The resulting temperature gradient ∇T in thermoelectric elements **24**, **30** may in turn cause each thermoelectric module **22** to generate a voltage. The electrodes **36**, **38** of thermoelectric modules **22** may be configured to electrically couple the thermoelectric modules **22** in a series configuration so that the voltages generated by the thermoelectric modules **22** add constructively to generate an output voltage V that causes a current I to flow through an electrical load **62** coupled to output terminals **64**, **66** of thermoelectric generator **52**.

FIG. **6** depicts a thermoelectric element **70** having a transverse geometry that utilizes the Nernst effect to generate a voltage from a temperature difference ΔT. The thermoelectric element **70** may include a height dimension h that generally corresponds with an x-axis of a three-dimensional coordinate system **72**, a length dimension l that generally corresponds with a y-axis of coordinate system **72**, and a width dimension w that generally corresponds with a z-axis of coordinate system **72**.

To generate a voltage V across the length l of thermoelectric element **70**, the Nernst effect requires a force that urges charge carriers in a direction orthogonal (i.e., perpendicular) to the temperature gradient ∇T produced by temperature difference ΔT across the element, e.g., orthogonal to the height h of thermoelectric element **70**. In conventional devices, this force is a Lorentz force resulting from the cross-product of the temperature gradient ∇T and a magnetic field H applied in a direction orthogonal to both the temperature gradient ∇T and the voltage gradient ∇V generated by the device. For the thermoelectric element **70** depicted in FIG. **6**, this magnetic field H may be generally parallel to the z-axis of coordinate system **72**.

As carriers move toward the cold side of the thermoelectric element **70** under the influence of the temperature gradient ∇T (as indicated by single headed arrow **71**), the magnetic field H may generate forces on the carriers that urge positive and negative charge carriers in opposite directions. For the depicted temperature difference ΔT and magnetic field H, this force may urge positive charge carriers in a positive direction along the y-axis and negative charge carriers in a negative direction along the y-axis. The movement of the charge carriers in thermoelectric element **70** under the influence of the temperature gradient ∇T and magnetic field H may thereby produce a voltage V across the thermoelectric element **70** having the shown polarity.

In contrast to the output of thermoelectric module **22**, which is limited by the intrinsic properties of the materials from which it is made, the output of thermoelectric element **70** scales with the size of the device. Advantageously, this allows the voltage V generated by thermoelectric element **70** to be scaled by simply adjusting its dimensions. Thus, thermoelectric generators based on this type of element may avoid the complexity of assembling a large number of thermoelectric elements as shown in FIG. **5**. However, because the magnetic field H required to generate useful amounts of electricity is typically quite large, conventional thermoelectric elements utilizing a transverse geometry and the Nernst effect are generally not suitable for power recovery from waste heat or other practical commercial applications.

Embodiments of the invention advantageously reduce or eliminate the need to provide a magnetic field H to thermoelectric elements utilizing the Nernst effect by using materials having a non-zero Berry curvature, such as certain Weyl semimetals. A Weyl semimetal is a solid-state crystal having low energy excitations that comprise Weyl fermions which carry electrical charge. It has been determined that Weyl semimetals having a non-zero integral over the Fermi surface of the projection of the Berry curvature Ω_z of the dispersion relation of their conduction electrons along a specific crystallographic axis can be used to create or increase Nernst thermopower α_{xyz}.

This property may enable materials having a non-zero Berry curvature to generate a thermoelectric voltage along a direction orthogonal to the direction of an applied temperature gradient without an externally applied magnetic field. Thermoelectric devices made using materials having a non-zero Berry curvature may be used to generate power and/or pump heat, and thus may have wide-ranging applications in many industries, such as the energy and electronics industries.

The origin of this thermoelectric effect is believed to lie in the presence of a non-zero Berry curvature of the electronic band structure at each electron energy and momentum value. A Berry curvature may be produced by an electronic band structure that exhibits spin-orbit canting, which may cause the material having the canted spin-orbit to exhibit a non-zero magnetic moment. The ability of a Weyl semimetal to generate voltages as described above may depend on the integral of the projection of the Berry curvature over the Fermi surface being non-zero. One way this may occur is when electrons in the solid break time-reversal symmetry. The Weyl nodes act as monopole sources (or sinks) of the Berry curvature. This Berry curvature acts as an effective magnetic field that exists in the electrons' momentum-space, introducing an anomalous velocity to electron motion that is skew to both the Berry curvature and the electrons' momentum. This skew force is believed to generate a non-zero thermoelectric power in a direction orthogonal to both the net Berry curvature integrated over the whole Fermi surface and the direction of the applied temperature gradient. This effect has been observed experimentally in the compound $YbMnBi_2$, which is a Weyl semimetal that breaks time-reversal symmetry and is a canted antiferromagnet material having a net Berry curvature Ω_Z along its [110] crystal axis.

By aligning the [110] crystal axis of a $YbMnBi_2$ crystal with the z-axis as depicted in FIG. **7**, the above described effect may be used to produce transverse thermoelectric devices, namely Nernst generators and their thermodynamic reciprocal, Ettingshausen coolers. Unlike classical Nernst generators and Ettingshausen coolers, thermoelectric devices made with materials having a non-zero Berry curvature do not require an external magnetic field H, the role of which is provided by the Berry curvature Ω_z. An external magnetic field can, however, still be applied, and its presence can be used to adjust (e.g., reinforce or counteract) the effect of the Berry curvature in certain circumstances.

Transverse thermoelectric devices such as shown in FIG. **7** have several advantages over classical Peltier devices, such as the thermoelectric modules and generator shown in FIGS. **4** and **5**. Because the electrodes applied to the thermoelectric material can lie in an isothermal plane of a transverse device, the electrodes can both be applied at either the hot end or the cold end of the device. That is, there is no need to return the current from the hot end to the cold end of the device. Thus, there is no need for a thermocouple pair, with a p-type material carrying the current from hot to cold and an n-type material carrying the current back from cold to hot.

Transverse thermoelectric devices have several advantages over conventional, longitudinal thermoelectric devices. For example, there is no need to simultaneously develop n-type and p-type thermoelectric materials with similar temperature dependences in their zT values. One material with one polarity suffices for the entire device. Another advantage is that there is no need to connect several thermocouples together electrically in series and thermally in parallel as must be done in thermoelectric modules and Peltier devices. Rather, in Nernst generators and Ettingshausen coolers, the current capacity and the voltage rating can be increased by simply increasing the physical size of the thermoelectric material in the device. More advantageously, having one pair of current contacts and one pair of thermal contacts may allow the parasitic losses in contact resistances of thermoelectric modules and Peltier devices to be decreased as compared to Seebeck effect-based devices using series electrical couplings.

The temperature difference in classical Peltier devices may be limited by the following equation:

$$\Delta T_{max}=\tfrac{1}{2}\times(zT\times T_{cold}) \quad \text{Eqn. 3}$$

Therefore, when larger temperature drops are required in a Peltier device, several Peltier elements are typically connected in cascaded coolers. This increases the complexity of devices aimed at generating cooling over large temperature gradients, especially in cryogenic cooling applications. However, these limitations in the maximum temperature gradient do not hold for Nernst/Ettingshausen devices. Therefore, Nernst/Ettingshausen devices can operate with large temperature gradients without cascading series connections.

The large transverse Nernst thermopower α_{xyz} of Weyl semimetals has been demonstrated experimentally using $YbMnBi_2$. The peak in the Nernst thermopower α_{xyz} of $YbMnBi_2$ in the absence of a magnetic field is approximately 1000 μV/K near 50K and 30 μV/K near room temperature. By way of comparison, commercially available thermoelectric materials have a Seebeck coefficient α_{xxz} near 200-300 μV/K at room temperature. The transverse thermoelectric figure of merit zT may be calculated using Equation 4 below:

$$zT_{xy} = \frac{(\alpha_{xyz})^2 \times \sigma_{yy}}{\kappa_{xx}} \times T \quad \text{Eqn. 4}$$

where α_{xyz} is the Nernst thermopower, σ_{yy} is the electrical conductivity in the direction parallel to the measured voltage, and κ_{xx} is the thermal conductivity in the direction parallel to the applied and measured temperature gradient.

For $YbMnBi_2$, the transverse zT in the absence of a magnetic field is estimated to be 2.42 at 59.55 K. This value is greater than that of any other known thermoelectric for this low of a temperature range, and for a transverse geometry (i.e. Nernst or Ettingshausen geometry) at any temperature. The performance of this new thermoelectric material, which is based on new physical principles, enables the novel approach to solid-state cryogenic cooling provided by embodiments of the invention, and may be useful in numerous cooling applications. For example, a number of detectors including infra-red detectors, focal plane arrays, and x-ray and gamma-ray detectors, could benefit from Ettingshausen coolers using thermoelectric elements having a non-zero Berry curvature.

FIG. **8** depicts an exemplary thermoelectric device **80** in accordance with an embodiment of the invention. The thermoelectric device **80** may include a thermoelectric element **82** comprising a material having a non-zero Berry curvature, a thermal coupler **84** configured to couple a hot side **86** of the thermoelectric element **82** to a heat source **88**, and a thermal coupler **90** configured to couple a cold side **92** of the thermal element to a heat sink **94**. The thermoelectric element **82** may be configured so that an axis of the material having the non-zero Berry curvature is generally orthogonal to the temperature and voltage gradients. Voltage output sides **96**, **98** of thermoelectric element **82** may be electrically coupled to respective terminals **100**, **102** to facilitate connection of the thermoelectric device **80** to an electrical load **104**. The thermoelectric device **80** may also include one or more magnets **106**, **108** configured to provide a magnetic flux **110** to the thermoelectric element **82**. The magnetic flux **110** may enter and exit the thermoelectric element **82** through the remaining sides **112**, **114**, and may be generally aligned with the axis having the non-zero Berry curvature. The magnetic flux **110** may be used to adjust (e.g., reinforce or counteract) the effect of the Berry curvature, thereby providing a mechanism for controlling the output and/or efficiency of the thermoelectric device **80**.

EXPERIMENTAL RESULTS

FIG. **9** depicts a test device **120** including a thermoelectric element **122** comprising $YbMnBi_2$. The thermoelectric element **122** is affixed to a silicon substrate **124**. The thermoelectric element **122** includes an outward facing surface **126** having a rectangular shape that faces away from the substrate **124**, and a downward facing surface (not shown) generally parallel to and spaced about 0.44 mm from the outward facing surface **126**. The thermoelectric element **122** is oriented so that the [110] crystal axis of the $YbMnBi_2$ (and thus the non-zero Berry curvature) is orthogonal (i.e., normal) to the outward and downward facing surfaces, e.g., projecting outward from the outward facing surface **126**. The rectangular shape of outward facing surface **126** is defined by a left facing surface **127**, a right facing surface **128** generally parallel to and about 2.58 mm from the left facing surface **127**, a top facing surface **129** that intersects the left and right facing surfaces **127**, **128**, and a bottom facing surface **130** generally parallel to and 1.85 mm from the top facing surface **129**. Each of the surfaces **127-130** is generally orthogonal to the outward facing and downward facing surfaces so that the thermoelectric element **122** generally forms a polyhedron having six sides and dimensions of 0.44 by 1.85 by 2.58 mm.

The left facing surface **127** of thermoelectric element **122** is thermally coupled to a resistive heater **136** by a copper foil heat spreader **138**. The heat spreader **138** is configured to provide heat generated by the resistive heater **136** evenly to the left facing surface **127** of thermoelectric element **122**. The right facing surface **128** of thermoelectric element **122** is coupled to a copper foil heat sink **140**. When the resistive heater **136** is energized, a temperature gradient forms having a decreasing temperature across the thermoelectric element **122** from the left facing surface **127** to the right facing surface **128**. A gold-plated copper bracket **142** attached to (e.g., epoxied to) the heat sink **140** and substrate **124** holds the test device **120** in place with respect to the substrate **124**. A clamp **146** holds the bracket **142** in place relative to a base **144** so that the substrate **124** is suspended above the base **144**. The bracket **142** is in thermal contact with the heat sink **140**, and thermally and electrically isolated from the base **144**. Insulated copper leads **148**, **150** electrically couple the top and bottom surfaces **129**, **130** to respective terminals **152**, **154** that facilitate measuring voltages V and/or currents I generated by or provided to the thermoelectric element **122**.

FIG. **10** depicts a graph **160** including plots **162-168** of the Nernst thermopower α_{xyz} in μV/K verses magnetic field strength H in Oersteds (Oe). The data used to define plots **162-168** was measured using the test device **120** at sample temperatures of 15.86 K (plot **162**), 23.17 K (plot **163**), 41.48 K (plot **164**), 59.44 K (plot **165**), 75.15 K (plot **166**), 118.4 K (plot **167**), and 323.1 K (plot **168**). The plots **162-168** illustrate the Nernst Effect in $YbMnBi_2$. The magnetic field was applied along an axis orthogonal to the outward facing surface **126** of thermoelectric element **122**, which is aligned with the [110] crystallographic axis and is thus the direction of the expected non-zero Berry curvature. Positive values of H indicate the field is oriented in an outward facing direction with respect to the outward facing surface **126** as depicted in FIG. **8**. As can be seen from plot **128**, the Nernst thermopower α_{xyz} has a non-zero value in the absence of an externally applied magnetic field that is significantly larger than that produced by conventional thermoelectric materials.

FIG. **11** depicts a scatter plot **180** including data points **182** illustrating the Nernst thermopower α_{xyz} in μV/K verses the temperature of the thermoelectric element **122** in kelvin for a transverse geometry (i.e., produced by the Nernst effect), and data points **184** illustrating the Seebeck coefficient α_{xxz} in μV/K verses the temperature of the thermoelectric element **122** in kelvin for a longitudinal geometry (i.e., produced by the Seebeck effect) in the absence of an externally applied magnetic field. The data points **182**, **184** were extracted from data taken without an externally applied magnetic field. In the absence of a Berry curvature, the Nernst thermopower α_{xyz} indicated by data points **182** would be expected to be 0 μN/K at all temperatures. Thus, the non-zero values shown for the Nernst thermopower α_{xyz} indicate the presence of a Berry curvature and confirm the effect of the Berry curvature on the Nernst thermopower α_{xyz}, which is significantly larger than would be expected for conventional thermoelectric materials configured in a transverse geometry. The disparity between the coefficients α_{xyz} and α_{xxz} produced by the Nernst and Seebeck effects support the conclusion that a non-zero Berry curvature produces the Nernst effect even in the absence of an externally applied magnetic field.

The conventional thermoelectric figure of merit, zT, may be calculated using Equation 5 below:

$$zT = \frac{\alpha_{xx}^2 \times \sigma_{xx}}{\kappa_{xx}} T = \frac{\alpha_{xx}^2}{\kappa_{xx}\rho_{xx}} \quad \text{Eqn. 5}$$

where ρ_{xx} is the resistivity of the thermoelectric material. The maximum value of zT known by the Applicant to have been measured in a laboratory is 2.2 at 915 K. The transverse figure of merit zT may be calculated using Equation 6:

$$zT_{xy} = \frac{\alpha_{xy}^2 \times \sigma_{yy}}{\kappa_{xx}} T = \frac{\alpha_{xy}^2}{\kappa_{xx}\rho_{yy}} = \frac{\alpha_{xy}^2}{\kappa_{xx}\rho_{xx}} \quad \text{Eqn. 6}$$

FIG. **12** depicts a scatter plot **190** including data points **192-194** showing figures of merit zT for different thermoelectric materials in the absence of an external magnetic field. Data points **192** illustrate the transverse figure of merit zT verses temperature in kelvin for $YbMnBi_2$ in a Nernst/Ettingshausen configuration. Data points **193** illustrate the longitudinal figure of merit zT verses temperature in kelvin for PbTe doped with 2 mol % Na and nanostructured with 4 mol % SrTe. Data points **194** illustrate the longitudinal figure of merit zT verses temperature in kelvin for commercially available Bi_2Te_3.

The depicted properties of $YbMnBi_2$ provide experimental support for the improved performance of thermoelectric devices in accordance with embodiments of the invention. Use of materials having a non-zero Berry curvature, such as $YbMnBi_2$, in fabricating thermoelectric devices allows a simpler transverse geometry that operates without an externally applied magnetic field. Moreover, the peak zT of $YbMnBi_2$ occurs in a temperature range appropriate for cooling (e.g., zT=2.42 at 59.55K). Thus, thermoelectric devices using materials such as $YbMnBi_2$ may be suitable for use in both power recovery applications and for heat pumps that cryogenically cool electronic devices.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the embodiments of the invention. As used herein, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, actions, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, actions, steps, operations, elements, components, and/or groups thereof. Furthermore, to the extent that the terms “includes”, “having”, “has”, “with”, “comprised of”, or variants thereof are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to the term “comprising”.

While all the invention has been illustrated by a description of various embodiments, and while these embodiments have been described in considerable detail, it is not the intention of the Applicant to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative apparatus and method, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the Applicant’s general inventive concept.

What is claimed is:

1. A thermoelectric device comprising:

a thermoelectric element having a first axis and including ytterbium manganese dibismuth ($YbMnBi_2$) having a non-zero Berry curvature along a [110] crystal axis thereof, the [110] crystal axis being aligned with the first axis, a first side, a second side located a first distance from the first side along a first dimension generally orthogonal to the first axis, a third side that intersects the first and second sides, and a fourth side located a second distance from the third side along a second dimension generally orthogonal to the first axis and the first dimension and that intersects the first and second sides;

a first thermal coupler configured to thermally couple the first side to one of a heat source or a heat sink;

a second thermal coupler configured to thermally couple the second side to the other of the heat source or the heat sink;

a first electrode electrically coupled to the third side; and

a second electrode electrically coupled the fourth side,

wherein an internally generated temperature gradient is generated between the first and second sides in response to passing an externally sourced current between the first electrode and the second electrode, and

a voltage is generated between the third and fourth sides in response to application of an externally sourced temperature gradient between the first thermal coupler and the second thermal coupler.

2. The thermoelectric device of claim **1** wherein the first axis of the material is orthogonal to the externally sourced temperature gradient to which the thermoelectric element is exposed or the internally generated temperature gradient the thermoelectric element generates.

3. The thermoelectric device of claim **1** further comprising:

a magnet configured to provide a magnetic field to the thermoelectric element.

4. The thermoelectric device of claim **1** wherein the thermoelectric device is one of an Ettingshausen cooler or a Nernst generator.

5. The thermoelectric device of claim **1**, wherein an external magnetic field is not applied to the thermoelectric element.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 11,011,692 B2
APPLICATION NO. : 16/157522
DATED : May 18, 2021
INVENTOR(S) : Joseph P. Heremans et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In the Specification

Column 4, Line 20, "FIG. 10 is graphical view illustrating the" should be --FIG. 10 is a graphical view illustrating the--.

Column 4, Line 24, "FIG. 11 is graphical view illustrating" should be --FIG. 11 is a graphical view illustrating--.

In the Claims

Column 14, Line 7, Claim 1, "a second electrode electrically coupled the fourth side," should be --a second electrode electrically coupled to the fourth side,--.

Signed and Sealed this
Twenty-first Day of September, 2021

Drew Hirshfeld
Performing the Functions and Duties of the
Under Secretary of Commerce for Intellectual Property and
Director of the United States Patent and Trademark Office